Ecological Services Anchorage Field Office

1 of 2 Reports

contened

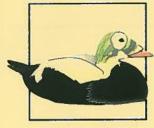
Technical Report WAES-TR-96-01



Habitat Conservation

Contaminant Case Report:

Spectacled Eider (Somateria fischeri) Eggs and Feathers from the Yukon-Kuskokwim Delta, Alaska



Endangered Species

by: Jean F. Cochrane Kimberly A. Trust



Environmental Contaminants

October 1996

CONTAMINANT CASE REPORT:

SPECTACLED EIDER (Somateria fischeri) EGGS AND FEATHERS FROM THE YUKON-KUSKOKWIM DELTA, ALASKA

Jean Fitts Cochrane and Kimberly A. Trust

October 1996

Ecological Services Anchorage Field Office 605 West 4th Avenue, Room G62 Anchorage, Alaska

Fish and Wildlife Service U.S. Department of the Interior

USFWS Technical Report WAES-TR-96-01

Content

	Page
Tables and Figures	ii
Summary	1
Introduction	2
Materials and Methods	3
Egg and Feather Collection	
Sample Preparation	3
Egg Harvesting and Shell Thickness (4); Feather Preparation (5)	4
Metal and Trace Florent Analysis	_
Metal and Trace Element Analysis	3
Quality Assurance/Quality Control (QA/QC)	5
Statistical Analysis	6
Results and Discussion	6
Quality Assurance/Quality Control	6
Egg Contaminant Residues	0
Feather Contaminant Residues	/
For Status	/
Egg Status	9
Egg Shell Thickness	10
Within Clutch Variability in Residue Concentrations	
The Callerina I	10
Egg Collection Location and Timing Effects	10
Correlation Between Feathers and Eggs from Same Nest	11
Individual Element Concentrations	11
Aluminum (11); Boron (11); Cadmium (11); Copper (12); Iron (12); Lead (12)	2):
Magnesium (13); Manganese (13); Mercury (13); Selenium (14); Strontium (13)	ĺ 5):
Zinc (15)	,,
Conclusion	1.5
	13
Acknowledgments	17
Literature Cited	

Tables and Figures

	Page
Egg and feather collection locations, Yukon-Kuskokwim Delta, Alaska	4
Mean concentrations (ppm dry weight) of inorganic elements in spectacled eider eggs from the Yukon-Kuskokwim Delta, Alaska, 1992	8
Mean concentrations (ppm dry weight) of inorganic elements in spectacled contour feathers from the Yukon-Kuskokwim Delta, Alaska, 1992	8

Summary

We collected spectacled eider (Somateria fischeri) eggs and shed breast contour feathers from nests on the Yukon-Kuskokwim Delta, Alaska, in 1992 to evaluate baseline contaminant levels. Samples came from representative regions on the Delta's outer coast both during and following incubation. We present data on inorganic element concentrations from eight feather samples and 21 eggs. Mercury levels were very low and selenium levels were somewhat elevated, although still below levels clearly identified with adverse effects on waterfowl reproduction. Eggs and feathers are inappropriate indicators for lead and cadmium exposure, and reference guidelines are not available for comparison with the copper and zinc levels we detected. Levels of most other trace elements were either below detection or below concentrations of concern. Organochlorine pesticide and PCB analyses did not meet quality assurance guidelines and are not reported.

Disclaimer: The mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Federal Government.

Introduction

This study provides baseline data on contaminant levels in the Yukon-Kuskokwim Delta breeding population of spectacled eiders (Somateria fischeri). We collected eggs and feathers from nests in three parts of the Delta, both during and following incubation, and considered possible differences between sites and egg status before reporting overall mean contaminant concentrations. We chose to collect eggs and feathers for this preliminary contaminants survey because these media are relatively easy to obtain and provide more representative data than salvaged carcasses. Additionally, their collection is less harmful to the population than collecting live birds, and eggs are a preferred substrate for assessing organochlorine pesticide exposure. Egg and feather samples, however, are not useful for assessing some metals and trace elements.

Sea ducks are known to accumulate high concentrations of nonessential metals such as cadmium. Nutrient elements, however, are usually not notably higher in sea ducks than in other ducks residing in the same areas (Ohlendorf et al. 1986). Cadmium and mercury levels are elevated in various marine species in the North Pacific (Ohlendorf 1993), yet scientists do not know whether this is due to recent anthropogenic sources and whether these elements are harmful at recorded concentrations. Selenium is another element of concern for waterfowl and lead poisoning from ingesting waste lead shot has killed eiders on the Yukon-Kuskokwim Delta (Franson et al. 1995). Cadmium, mercury and selenium may pose the greatest threat to diving sea ducks (Ohlendorf et al. 1991). These elements, including lead, can have synergistic effects and their toxicity can also be influenced by body burdens of zinc and cooper (Ohlendorf et al. 1991). Therefore, levels of these elements should be considered in tandem.

Elimination of metals and trace elements can occur through excretion or through sequestration in feathers or eggs (Ohlendorf 1993). Feathers are useful depositories for contaminants, because normally they are molted and re-grown at least once a year. However, some trace elements may adhere to feathers through external contamination or be reduced through leaching, which complicates interpretations of the bird's exposure to these contaminants. Different kinds of feathers from the same bird may also contain different concentrations of trace elements, depending partly on when and where the feathers were grown during the molt cycle. Washing feathers in deionized water can remove exogenous minerals on feather surfaces, but leave endogenous residues that reflect exposure during feather growth (Edwards and Smith 1984). If considered carefully, feathers may be good indicators of exposure to certain elements including arsenic, mercury and selenium.

Female birds sequester some metals in their eggs. Mercury and selenium concentrations in bird eggs reflect exposure of the female to those elements (Ohlendorf 1993). However, eggs are not considered useful for assessing exposure of birds to aluminum, boron, cadmium or lead because very little of these elements transfers to eggs regardless of dietary levels that birds consume. Although some lead is transferred to eggs (primarily in shells)

concentrations are typically low and variable and they do not correlate well with dietary exposure (ibid). Cadmium, lead and mercury are best measured in liver and kidneys (Ohlendorf 1993). Egg accumulations of nickel, chromium, molybdenum and vanadium have not been studied.

All analytical results in this report are expressed in parts per million (ppm) on a dry-weight (dw) basis for eggs and "as-received" basis for feathers, unless indicated otherwise. Where necessary for discussion, we convert contaminant concentrations that were reported on a wetweight (ww) basis in published literature to dry-weight values using moisture contents supplied by authors or by assuming an average egg moisture content of 70%.

Materials and Methods

Egg and Feather Collection

We collected eggs from spectacled eider nests on the Yukon Delta National Wildlife Refuge, Alaska, during June and July, 1992. Eggs were taken from nests found during mid-June nest searches at three study sites on the Yukon-Kuskokwim Delta: Hock Slough (Lower Kashunuk River), Kigigak Island, and random plots on the north side of Hazen Bay (Aprothluk and Opagaruk Rivers) (Fig. 1). The darkest (presumably the oldest) egg was selected from each clutch, except at one nest where the three darkest eggs were selected to investigate intra-clutch variability. Biologists working at the Hock Slough and Kigigak Island sites also collected eggs that failed to hatch from additional nests in late June and early July.

Eggs were handled with clean latex gloves, wrapped in aluminum foil and packed in individual foam-filled containers. A sample of breast contour feathers (usually 4-10 feathers) was pulled from the nest material at each nest, placed in a clean plastic bag, labeled externally, and placed inside the lid of the egg container. Eggs from Hock Slough were refrigerated in field camp and air shipped to Anchorage after 5-7 days. Containers with eggs from Hazen Bay and Kigigak Island were placed in the ground resting on permafrost, for up to six days until transport to U.S. Fish and Wildlife Service's Kanagyak field camp where they were refrigerated before air transport to Anchorage.

The unhatched eggs were wrapped, packaged and shipped similarly to the eggs collected in mid-incubation, but were held for varying periods before transfer to Anchorage. Before collection, the unhatched eggs had been candled about weekly to monitor development and labeled directly on the shell with an indelible pen. In Anchorage, eggs were kept under refrigeration for 4-10 weeks before harvesting.

Fig. 1. Egg and feather collection locations, Yukon-Kuskokwim Delta, Alaska.

Sample Preparation

Egg Harvesting and Shell Thickness

In the laboratory, eggs were weighed and egg length and width were measured to the nearest 0.01 mm with a dial gauge micrometer. Egg volume was estimated by the equation:

$$V = K_v * LB^2$$

Where K_v = the common volume coefficient 0.51 (Stickel et al. 1973, Hovt 1979), L = egg length, and B = egg breadth.

We harvested eggs by scoring at the equator with a scalpel and emptying the contents directly into chemically-clean glass jars. A new scalpel blade was used for each egg, after rinsing with acetone and distilled water. We recorded apparent fertility and stage of embryo

development, putrefaction, color, and other characteristics of each egg. Egg contents were frozen immediately and shipped on dry ice to the Hazleton Environmental Services, Inc. laboratory in Madison, Wisconsin. The egg samples were weighed and homogenized before analysis; sample moisture content was estimated by weight loss after freeze drying.

We left shell membranes in the shell where possible and let the egg shells dry in open air for 6-7 weeks. Then we measured shell thickness to the nearest 0.01 mm with a dial gauge micrometer at 10 points on the equator and averaged the measurements for each egg.

Feather Preparation

3

In the laboratory, we handled the feathers with latex gloves, weighed each sample to the nearest 0.01 gm, rinsed them by pouring distilled water over the feathers, and placed them in chemically-clean glass jars. Feathers were not "washed" in solution, soaked or agitated and they were not dried before placement in jars. Each nest was a separate sample. Feather samples were shipped to the Hazelton laboratory. Feather samples were weighed and homogenized before analysis; moisture content was not estimated.

Metal and Trace Element Analysis

Metal and trace element analyses were completed at the Hazelton Laboratory. Aluminum, boron, barium, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, strontium, vanadium and zinc were analyzed by inductively coupled plasma emission spectroscopy following nitric acid digestion. Mercury analysis was conducted using cold vapor atomic absorption spectroscopy following sulfuric and nitric acid digestion. Mercury was reduced with sodium borohydride for determination. Graphite furnace atomic absorption spectroscopy was used to analyze samples for arsenic, cadmium, lead and selenium following nitric acid digestion.

Quality Assurance/Quality Control (QA/QC)

Data were screened for acceptable QA/QC values based upon the following criteria (Quakenbush and Snyder-Conn 1993):

1. Precision, as measured by comparison of duplicates, was quantified by determining a relative percent difference (RPD) using the following formula:

$$RPD = ([D_1 - D_2]/([D_1 + D_2]/2)) * 100$$

where, D_1 = concentration measured in the first analysis and D_2 = concentration as measured in the second analysis.

Acceptable average precision for samples with both duplicate values greater than twice the limit of detection was $\leq 20\%$.

- 2. Maximum concentration of each analyte allowed in the procedural blank was $\leq 15\%$ of the mean sample concentration reported in the duplicate analysis.
- 3. Average spike recovery was acceptable between 80-120%.
- 4. Average standard reference material recovery was required to be within three standard deviations of the certified value. If no standard deviation was available, the standard deviation was assumed to be $\pm 10\%$ of the certified value.

Statistical Analysis

We used SAS statistical software (SAS Institute, Inc. 1985) univariate, correlation analysis, t-test, and multivariate analysis of variance (ANOVA) procedures to generate summary statistics and comparisons between egg subsamples and between eggs and feathers. Before analysis, we examined data for normality, kurtosis and skewness. A log_n transformation of the data was necessary to normalize distribution and reduce heterogeneity of variance. Means and standard deviations reported in the tables were computed from non-transformed data.

We used t-tests to compare differences in mean element concentrations between viable and non-viable eggs and to test for equal variance in element concentrations between same-clutch and unrelated eggs. We used two-way and multivariate ANOVA for comparing element concentrations by egg status, collection location and collection timing. Element concentrations in eggs were compared with feathers from same nests using correlation analysis. Results reported as significant differences had p values < 0.05.

Results and Discussion

During mid-June, we collected 10 eggs and eight feather samples from eight nests (one egg each from two nests on random plots, three nests at Kigigak Island and five eggs from three nests at Hock Slough; hereafter "mid-incubation" eggs). After hatching was complete, biologists collected eggs that did not hatch from five Hock Slough nests (five eggs) and two Kigigak Island nests (seven eggs) (hereafter "unhatched" eggs). The mean moisture content was 68% in the mid-incubation eiger eggs and 65% in unhatched post-incubation eggs. Moisture content was not determined for the feathers.

Quality Assurance/Quality Control

All elements except arsenic and cadmium met QA/QC criteria. Arsenic concentrations barely exceeded detection limits. Additionally, arsenic spike recoveries were only 80-83% and percent relative difference in arsenic duplicate samples was 67-86%; thus, arsenic results are not included in this report. Similarly, cadmium concentrations were barely detectable

and cadmium spike recoveries were only 73-83%. We expected cadmium concentrations to be low or below detection, because this metal does not accumulate in eggs or feathers. Thus, the cadmium results are consistent with our expectations, despite the low spike recovery.

Organochlorine analysis of egg samples did not meet Fish and Wildlife Service QA/QC criteria because most spike recoveries were well below 80%. Due to the unreliability of these results, we do not discuss organochlorine compound data in this report. It should be noted that these organochlorine results were cited as primary data in Henny et al. (1995). They were published without our knowledge or review and, therefore, cannot be considered valid.

Egg Contaminant Residues

We report mean concentrations for inorganic elements that were detected in at least 50% of the samples. If >50% of samples had concentrations above detection limits then one-half the detection limit was assigned to the remaining below-detection samples when calculating means. Results for copper, iron, magnesium, manganese, mercury, selenium, strontium and zinc are presented for eggs in Table 1; average concentrations of manganese and mercury were barely above detection limits. Egg concentrations of the following elements were below detectable limits: aluminum, beryllium, boron, cadmium, lead, molybdenum, nickel and vanadium. Chromium (0.90 ppm) was detected only in one addled egg from Kigigak Island and barium was detected in less than half of the samples¹.

Feather Contaminant Residues

Results for aluminum, boron, copper, iron, magnesium, manganese, mercury, selenium, strontium and zinc are presented for breast contour feathers in Table 2; because detection limits were high we do not report mean values. Feather samples were small (0.03-0.42 g). Beryllium, cadmium, chromium and molybdenum were not detected in the contour feathers from nests, while barium, nickel and vanadium were each detected in only one feather sample from a Hazen Bay nest².

¹1. Detection limits for elements detected in <50% of samples: Al (2.5-3.5), As (.03-.07), Ba (.51-.72), Be (.05-.07), B (1.03-1.43), Cd (.16-.21), Cr (.26-.36), Pb (1.27-1.66), Mo (1.02-1.41), Ni (.31-.42) and Vn (.13-.18).

²1. Detection limits for elements detected in <50% of samples: As (.01), Ba (.20-33.3), Be (.1-3.3), Cd (.29-10.0), Cr (.48-16.7), Pb (1.6-83.3), Mo (1.9-66.7), Ni (.12-20.0) and Vn (.05-8.3).

Table 1. Mean concentrations (ppm dry-weight) of inorganic elements in spectacled eider eggs from the Yukon-Kuskokwim Delta, Alaska, 1992.

	Detection		All Eggs (n = 2	21)¹
Element	Limit (ppm)	mean	s.d. ²	range
Cu	0.26-0.36	4.60	1.02	3.11-7.1
Fe	2.6-3.6	123.1	39.1	46.4-230.5
Mg	2.6-3.6	357.5	42.0	266-462
Mn	0.26-0.36	1.25	0.42	0.52-2.35
Hg	0.03-0.33	0.16	0.08	0.07-0.36
Se	0.26-0.36	3.55	0.67	2.18-5.27
Sr	0.13-0.18	12.7	3.66	6.43-19.9
Zn	0.51-0.72	46.0	7.61	31.3-66.6

^{1.} Validity of using 21 eggs for mean determination discussed in text.

Table 2. Concentration ranges (ppm dry-weight) of inorganic elements in spectacled eider contour feathers from nests on the Yukon-Kuskokwim Delta, Alaska, 1992.

Element	Detection Limit	Contour Feather Samples
	(ppm)	$(n = 8)^1$
Al	1.00	90.7-396
В	0.40	18.3-312
Cu	0.10	27.7-119
Fe	1.00	205-734
Mg	1.00	224-1010
Mn	0.10-6.25	3.1-66.2
Hg	0.01	0.04-0.40
Se	0.10	21.3-75
Sr	0.05	3.04-15.7
Zn	0.20	24.6-167

^{1.} n = 8 nests; feathers pooled for nest.

^{2.} Standard deviation.

Egg Status

Of the 10 eggs collected during mid-June, four eggs (from two nests) had developed to approximately mid-incubation indicating viability at time of collection and five eggs were rotten (the condition and color of rotten egg contents varied considerably). In the 10th egg, embryonic development was less than five days, indicating probable death before collection even though the egg was not rotten (most eider nest incubation began about 10 days pre-collection at these nests). Thus, for statistical analysis we classed the mid-incubation eggs as 5 non-viable and 5 viable.

Of the 12 unhatched eggs collected after incubation, 11 were non-viable. Nine of the 11 unhatched/addled eggs were either infertile or too rotten to determine stage of development, one had developed to less than five days and one to mid-incubation. The only fully-developed egg was cracked at collection and is omitted from average contaminant concentrations reported here. For statistical analysis we classed the 11 whole, unhatched eggs as non-viable.

We evaluated possible differences in element concentrations between non-viable and viable eggs through multivariate and individual ANOVA. The geometric mean copper concentration was higher in non-viable than in viable eggs (p = 0.03), but the slight difference (0.67 v.s. 0.61 ppm; n = 16 and 5) is probably not meaningful biologically. Differences in the geometric mean values for nine other element concentrations were not detected based on egg status (p > 0.05 for Ar, Ba, Fe, Hg, Mg, Mn, Se, Sr, and Zn). Thus, we report the average values from non-log transformed data for all 21 eggs in Table 1.

Excessive amounts of cadmium, lead, mercury, selenium or zinc in the diet can reduce reproductive success of birds (Eisler 1985a, 1985b, 1988, 1993, Scheuhammer 1987, Ohlendorf 1993). "The embryo is often the most sensitive life stage and hatchability of eggs may be affected by contaminants at concentrations much lower than those that cause observable effects in adult birds. Post-hatching survival of chicks also may be reduced by contaminant burdens they received in the egg" (Ohlendorf 1993:236). Embryotoxicosis may affect some but not all eggs in a clutch (Ohlendorf et al. 1989).

Chronic exposure to lead and other contaminants may affect female behavior and nest attentiveness, leading to egg failure without direct contamination of the egg (D. Hoffman, National Biological Service, pers. comm.). Ohlendorf (1993) recommended cause-specific studies of hatchability and nest failure, because aquatic birds affected by environmental contaminants may experience partial clutch failure even though nest success in general does not decline. Although our sample is too small to shed light on rates of egg addling in the population, it contributes to concerns that the frequency of spectacled eider egg addling may have increased since the early 1970s (C. Dau, U.S. Fish and Wildlife Service, pers. comm.).

Egg Shell Thickness

The shells of some unhatched, addled eggs (n = 4) were brittle and cracked during harvesting. We measured shell thickness on nine mid-incubation nest eggs (from seven nests) and three unhatched eggs. Shell thickness averaged 0.29 mm in mid-incubation nest eggshells (n = 7 nests) and 0.30 in unhatched eggshells (n = 3 nests) (multi-egg clutches were pooled before averaging). Comparison data are not available on historical eggshell thickness or on organochlorine concentrations that may affect shell thickness in spectacled eiders.

Within Clutch Variability in Residue Concentrations

One assumption of sample-egg contaminant studies (analysis of one egg per nest) is that occurrence and concentrations of contaminants are similar among eggs within a clutch (Ohlendorf 1993). Available data, mostly on organochlorines, generally support this assumption, but more information is needed for trace elements (Ohlendorf 1993). Birds rid themselves of body burdens of some elements by sequestration into eggs and feathers, thus, residue concentrations can vary by egg laying or feather molt sequence. For example, Heinz et al. (1989) reported that selenium concentrations differed little between mallard eggs within clutches from hens on low dietary doses. But at high dietary doses, differences between eggs were nearly significant for selenomethionine (decreased with time) and were significant for selenocystine, which increased with time. Stage of embryo development may also affect residue levels of some elements in eggs.

To test for intra-clutch variability in spectacled eiders, we compared the variability in element concentrations between eggs collected mid-incubation from a single nest (n=1 nest, 3 eggs) with eggs collected mid-incubation from different nests (n=7 nests, 7 eggs). Concentrations of mercury (p=0.03) and strontium (p=0.02) were significantly less variable within the single clutch than among the seven unrelated clutches (2-tailed t-tests). However, Hg concentrations were close to detection limits where error is normally high and in both Hg and Sr, mean values were not significantly different between individual eggs and same-clutch eggs (p>.24 and .68, respectively). For copper, iron, magnesium, manganese, selenium and zinc, however, the three eggs from a single nest were as variable as those from multiple nests (n=10, 2-tailed t-tests, p>0.10 for all six elements), indicating that the assumption of low within-clutch variability may not be valid.

Egg Collection Location and Timing Effects

We tested for differences in copper; selenium,-strontium and zinc concentrations³ between egg collection locations (Hoch Slough, Kigigak Island and Hazen Bay) and between collection timing (mid-incubation and unhatched post-incubation eggs) using multivariate ANOVA. The

³ Elements that had concentrations well above detection limits in eider eggs and that may be of greater concern due to possible health or interactive effects.

geometric mean concentrations in eggs did not differ between collection sites (n = 21, p > 0.10 for each element) or collection method (n = 21, p > 0.10 for each element).

Correlations Between Feathers and Eggs from Same Nest

We tested for correlations between element concentrations in same-nest samples of eggs (n = 8 nests) and contour feathers. We found no correlation for Cu, Fe, Mg, Mn, Hg, Se, Sr and Zn (Pearson correlation p > 0.10 for each element; other elements were below detection limits in one or both sample media).

Individual Element Concentrations

Results are reported as the range and arithmetic mean of concentrations for 21 eggs and range for eight feather samples (Tables 1 and 2, respectively).

Aluminum

Aluminum has a low potential for toxicity in birds, as birds effectively limit absorption and excrete excess concentrations (Scheuhammer 1987). Reproductive effects of high dietary aluminum have not been demonstrated. Aluminum levels were below detection in all spectacled eider egg samples and averaged 178.9 ppm (range 90.7-396 ppm) in contour feathers from the Yukon-Kuskokwim Delta.

Boron

Boron is ubiquitous in natural environments and is elevated in the atmosphere from human activities (agricultural runoff, mining, coal burning) (Eisler 1990). Boron is a potent teratogen in chickens and it affects mallard (*Anas platyrhynchos*) growth, behavior and brain biochemistry (Eisler 1990). Guidelines are not available for interpreting how boron feather concentrations may affect eider health. Boron was below detection level in spectacled eider eggs and ranged from 56.9 to 200.0 ppm in contour feathers.

Cadmium

Cadmium is a relatively rare heavy metal with no known biological function. It is teratogenic, carcinogenic and probably a mutagen (Eisler 1985a). Anthropogenic sources in the environment include smelting, coal and oil burning, fertilizers, and waste incineration and wastewaters; hence, concentrations are highest near industrial sources. Marine aquatic organisms accumulate cadmium from water and they generally contain substantially higher residues than do their non-marine counterparts.—Sublethal effects in birds include growth retardation, suppressed egg production, egg shell thinning, altered behavioral responses and others (Scheuhammer 1987, Furness 1996). Elevated cadmium concentrations affect iron, zinc and copper metabolism and concentrations in bird tissues (Furness 1996). Zinc, iron, calcium and selenium ameliorate cadmium's effects, however, while lead and mercury exacerbate them (Eisler 1985a).

Very little cadmium transfers into eggs (Scheuhammer 1987, Leonzio & Massi 1989). Normal background level in bird eggs is <0.5 ppm dw and toxic (impaired health or reproduction) levels are not known (Ohlendorf 1993). Mallards fed various cadmium doses laid eggs averaging 0.01-0.04 ppm ww cadmium (White and Finley 1978). It is not clear whether feather cadmium concentrations result from dietary or exogenous exposure; therefore, feathers are not useful for monitoring dietary exposure (Furness 1996).

Elevated cadmium levels in spectacled eider carcasses found in western Alaska in the early 1990s (up to 335 ppm dw in kidneys, unpublished data) have raised concerns about possible cadmium effects on these sea ducks. Cadmium was below detection levels in the spectacled eider eggs and contour feathers we collected from nests. The detection limits for cadmium in our egg samples (0.16-0.21 ppm) were higher than the cadmium concentrations observed in eggs from Mallards fed cadmium (White and Finley 1978). Further, since cadmium concentrations in eggs and feathers remain low despite high dietary cadmium (Scheuhammer 1987, Furness 1996), we can learn little about spectacled eiders' exposure to cadmium from the data in this study.

Copper

Copper is an essential trace element that is regulated metabolically by organisms (Ohlendorf 1993). Copper exacerbates the toxic effects of lead (Eisler 1988). Toxicity reference values for copper levels in sea duck eggs are not available. Common eiders (Somateria mollissima) in a Norwegian fjord polluted with copper and zinc from mining effluent accumulated an average of 4 ppm dw copper in their eggs (Lande 1977). Mallard eggs from Moravia averaged 0.76 ppm dw copper (Hudec et al. 1988). Copper can contaminate feathers externally after their formation (Goede and de Bruin 1986). In our study, copper averaged 4.6 ppm (range 3.46-7.10 ppm) in eggs and ranged from 27.7 to 119 ppm in contour feathers.

<u>Iron</u>

Iron concentrations vary considerably among and within bird species, complicating interpretation of analytical results. Iron is an essential element and diving seabirds may require higher iron levels than other birds for oxygen storage. Guidelines are not available for interpreting iron levels in eider eggs or feathers. Common eider eggs collected by Lande (1977) in polluted Norwegian waters averaged 128 ppm dw iron. Iron can contaminate feathers externally after formation (Goede and de Bruin 1986). Spectacled eider eggs in our samples averaged 123.1 ppm iron (range 46.4-230.5 ppm) and contour feathers ranged from 205 to 734 ppm iron.

Lead

Lead is a non-essential, toxic element. It does not biomagnify in food chains, but body burdens can increase in older organisms (Eisler 1988). Ingestion of waste lead gunshot causes acute toxicity and absorption of low concentrations may result in a wide range of sublethal effects (Pain 1996). Spectacled eiders on the Yukon-Kuskokwim Delta have died from ingesting lead shotgun pellets (Franson et al. 1995). Lead may reduce hatching rate, lower growth rates and

cause behavioral abnormalities (Eisler 1988). The toxic effects of lead are exacerbated with excess body concentrations of cadmium, zinc, copper and mercury (Eisler 1988).

Lead concentrations are typically measured in liver, kidney, blood and bones (for lifelong exposure). Feathers may provide useful lead data, but lead does not transfer predictably into eggs (D. Hoffman, National Biological Service, pers. comm.). Normal background lead level is <0.5 ppm fw [<1.7 ppm dw] in eggs; toxic concentrations in eggs are not known (Ohlendorf 1993). Lead concentrations in feathers may increase considerably with time and exposure to external lead through secretion products of the bird (Goede and de Bruin 1986). It is unclear how dietary lead affects feather concentrations (Goede and de Voogt 1985, Eisler 1988).

Lead was not detected in our spectacled eider egg or feather samples from nests. Lead was above detection levels in a primary feather from one lead-poisoned spectacled eider carcass, but below detection in primaries of two other lead fatalities and in contour feathers of all three lead-poisoned eiders from the Yukon-Kuskokwim Delta.

Magnesium

Ð

Magnesium is a required nutrient in birds and toxicosis from excess magnesium has not been reported. The spectacled eiders eggs averaged 357.5 ppm (range 266.3-462.1 ppm) and contour feathers ranged from 224 to 1010 ppm.

Manganese

Manganese is another required element that is normally regulated homeostatically, but the effects of excess body burdens in wild birds are not known. The spectacled eider egg samples averaged 1.25 ppm (range 0.52-2.35 ppm) and contour feathers ranged from 3.13 to 66.2 ppm.

Mercury

Mercury is non-essential and toxic to most birds and it is rapidly biomagnified in food webs (Eisler 1987). The normal background mercury level in bird eggs is <1 ppm ww (about <3-4 ppm dw) (Eisler 1987, Ohlendorf 1993). In general, seabirds exhibit higher mercury concentrations than terrestrial birds (Thompson 1996). Egg mercury concentrations up to approximately 0.5 ppm ww (about 1.5-2.5 ppm dw) appear to have little detrimental effect on reproduction and toxicity thresholds in seabirds may be substantially higher (Thompson 1996).

Mercury accumulates in bird feathers and does not diminish with time (Braune 1987). Feather concentrations reflect the bird's body burden, rather than either dietary intake during feather formation or external contamination (Goede and de Bruin 1986, Furness et al. 1986).

Mercury in spectacled eider eggs averaged 0.16 ppm dw (range 0.07-0.36 ppm) and contour feathers ranged from 0.04 to 0.40 ppm-- low concentrations within normal background ranges for North Pacific seabirds.

Selenium

Selenium is a required micronutrient yet it is toxic at high dietary concentrations and it bioaccumulates through diet (Eisler 1985b). High concentrations result from naturally seleniferous rocks and soils, and from human activities (e.g., burning fossil fuels and smelting various metals). Toxicity in birds varies greatly with different chemical forms of selenium. Selenium metabolism is significantly modified by interaction with various heavy metals and other factors, such as dietary protein (Eisler 1985b, Hoffman et al. 1992). Dietary selenium can reduce the toxic effects of cadmium, copper, lead and mercury (Heinz 1996).

Selenium concentrations in feathers mostly reflect recent external exposure via preening and are closely related to recent body burden (Goede and de Bruin 1986). In contaminated birds, preen glands contain high selenium concentrations. Selenium does not bind firmly to keratin, however, and can wash off feathers.

Avian embryos are very sensitive to the toxic effects of selenium (Ohlendorf et al. 1989). Selenium concentrations both accumulate and decline rapidly in birds so egg concentrations best represent contamination of the local environment (Heinz 1996). Hatchability of fertile eggs is considered the most sensitive measure of selenium toxicity (Ohlendorf 1993, Heinz et al. 1989). Different forms of organic and inorganic selenium have markedly different effects on birds, however (Heinz et al. 1989, Hoffman and Heinz 1988) and forms of selenium in marine foods have not been studied (Heinz 1996). Up to 99.9% of selenium found in livers of spectacled eiders collected from St. Lawrence Island, Alaska was in the selenomethionine (organic) form (K. Trust, unpublished data).

The normal, background selenium level in bird eggs of various species is 1-3 ppm dw (Ohlendorf 1993). Various studies indicate selenium concentrations are higher in marine birds than other bird species (Ohlendorf et al. 1986), although concentrations in eggs of marine birds in the North Pacific were in the 1-3 ppm dw range (Ohlendorf 1993). A range of selenium concentrations is associated with reproductive problems so it is difficult to set a single threshold concentration for embryonic impairment in multiple species (Heinz et al 1989). Heinz (1996) suggests that about 3 ppm ww (9-12 ppm dw) selenium in eggs is a threshold for reproductive impairment (from studies of selenomethionine only).

Heinz et al. (1989) concluded that "when eggs of wild birds contain wet-weight concentrations of selenium >1 ppm [about 3.3-4.0 ppm dw], one should consider the possibility of reproductive impairment and look closely at the reproductive success of the birds in the area." Ruelle (1991) and Welsh and Mayer (1991) found selenium concentrations above background levels (3.6-13.0 ppm dw) in piping plovers (*Charadrius melodus*) and least terns (*Sterna alntillarum*) on the Missouri River. Ruelle (1991) concluded that, while these levels were below concentrations associated with teratogenesis and impaired hatchability elsewhere, they may be an "additive adverse impact to other environmental factors already inhibiting population growth [of these threatened and endangered species]."

In our study, selenium concentrations in spectacled eider eggs averaged 3.55 ppm dw (range 2.18-5.27 ppm), while contour feathers from nests ranged from 21.3 to 75 ppm. Selenium concentrations in kidneys and livers of spectacled eiders from the Yukon-Kuskokwim Delta were substantially elevated (up to 103 pm dw in kidney and 144 ppm dw in liver, unpublished data; selenium was even higher in spectacled eiders from the Bering Strait and Russia), exceeding tissue concentrations that cause reproductive problems in waterfowl (Heinz 1996). Guidelines are not available for interpreting the feather concentrations. The egg concentrations we detected are elevated, but are below levels clearly identified with adverse effects on reproduction.

Strontium

Elemental strontium, an alkaline earth metal, is poorly absorbed and is not known to be toxic in birds. A number of strontium compounds, however, are hazardous to fish and wildlife. No guidelines are available for concentrations in birds. In our samples, spectacled eider eggs averaged 12.7 ppm (range 6.43-19.88 ppm) and contour feathers ranged from 3.04 to 15.7 ppm.

Zinc

Zinc is a ubiquitous, essential trace element. At high concentrations, zinc is toxic and reduces fertility and hatchability in chicken eggs (Eisler 1993). Anthropogenic sources of zinc in the environment include smelting, mine drainage, sewage, and waste and fossil fuel combustion.

Zinc interacts with cadmium, chromium, copper, lead, mercury, nickel and selenium. In terrestrial animals zinc protects against lead and nickel toxicosis (Eisler 1993). Zinc also diminishes or negates the toxic effects of cadmium, except for some zinc-cadmium mixtures in aquatic organisms (Eisler 1993). In ducks, zinc interacts with cadmium with "serious implications for waterfowl stressed simultaneously with cadmium and zinc" (Brown et al. 1977 in Eisler 1993). In North Pacific seabirds, zinc levels correlated with cadmium levels (Ohlendorf 1993).

Guidelines are not available for interpreting zinc concentrations in bird eggs or feathers. Eisler (1993) reported zinc concentrations from eggs of various bird species ranging from 4.3 to 65 ppm dw. Eisler (1993) summarized average feather zinc concentrations from various birds species ranging from 38-977 ppm dw. Feathers may be contaminated externally, so feather residue results can be misleading (Goede and De Bruin 1986). Spectacled eider eggs we collected averaged 46.0 ppm dw (range 31.3-66.6 ppm) and contour feathers from nests ranged from 24.6 to 167 ppm--within the background levels for birds reported by Eisler (1993).

Conclusion

We did not find any significant differences between residue levels⁴ in eggs from three study sites: Hock Slough, Kigigak Island and Hazen Bay; however small sample size (n = 8 nests)

⁴For four elements of concern: Cu, Se, Sr and Zn.

precludes generalizing from this finding. We also did not find any differences in contaminant levels⁵ between eggs collected during incubation and unhatched eggs collected after incubation (n = 21 eggs). This result indicates that spectacled eider egg contaminant levels may be monitored adequately with unhatched ("addled") eggs. In contrast, our findings do not support using contour feathers to indicate exposure levels in eggs--none of the trace element concentrations⁶ in feathers correlated with concentrations in eggs from the same nests.

In companion work to this study, we found elevated lead and cadmium concentrations in eider carcasses from western Alaska. National Biological Service researchers have also documented lead shot ingestion in eiders on the Yukon-Kuskokwim Delta (Franson et al. 1995). This study does not shed light on population exposure and potential adverse effects of these elements because lead and cadmium pass minimally into eggs and feathers.

Mercury and selenium can be measured in eggs and feathers. Mercury residues in our study ranged from below detection to 0.2 ppm in eggs and below detection to 0.32 ppm in feathers from nests, both well below the threshold of concern. We conclude that the spectacled eiders we sampled had been exposed minimally to mercury.

Selenium concentrations were somewhat elevated in our egg samples. Selenium residues averaged 3.55 ppm dw in all eggs (n = 21) (range for individual eggs was 2.18-5.27 ppm). "Normal" or background selenium in eggs is thought to be 1-3 ppm ww (about 3.3-10 ppm dw) (Ohlendorf 1993). In eggs, selenium reflects very recent exposure of the laying hen. Selenium in spectacled eider contour feathers from mid-incubation nests averaged 42-64 ppm dw (n = 3). In feathers, selenium concentrations reflect primarily exogenous deposition from gland secretions during preening (recent exposure) and toxicity reference values are not available (Heinz 1996).

Zinc concentrations averaged 46 ppm dw in the spectacled eider eggs and 113 ppm dw in contour feathers. Copper concentrations averaged 4.6 ppm dw in eggs and 91 ppm dw in contour feathers. Levels of most other elements were either below detection (Al, Ba, Be, B, Cr, Mo, Ni, Vn) or below known levels of concern for birds (Mg, Mn). We do not know enough about how some trace elements and metals such as copper, iron, strontium and zinc affect seaducks to conclude how the observed concentrations may interact with other contaminants and affect spectacled eiders.

Based on this study, selenium and possibly copper appear to be somewhat elevated in spectacled eider eggs, but we do not know how these concentrations affect eider health and reproduction. In particular, we do not know whether existing selenium levels affect eider egg hatchability or duckling survival. Evaluating selenium's impact would be complicated by potential synergistic

⁵Cu, Se, Sr and Zn.

⁶Cu, Fe, Mg, Mn, Hg, Se, Sr and Zn.

effects of multiple contaminants found in spectacled eider tissues, including cadmium, copper, lead, strontium and zinc.

Acknowledgments

We thank Tom Fondell, Paul Flint, Barry Grand, Chris Harwood, Pat Heglund, Amy Maehler, Tina Moran, Margaret Petersen, and Bob Stehn for assisting with egg collection. Wayne Crayton and Mark Giger helped with egg harvesting and egg shell measurements, respectively. Yukon Delta National Wildlife Refuge staff, especially pilot George Walters, provided essential logistical support. Sonce de Vries assisted with catalog preparation and Martha Corey provided administrative support. Thanks to Amy Dellinger for statistical consultation and cheerfully running the SAS programs.

Literature Cited

- Braune, B.M. 1987. Comparison of total mercury levels in relation to diet and molt for nine species of marine birds. Archives of Environmental Contaminants and Toxicology 16:217-224.
- Edwards, W.R. and K. E. Smith. 1984. Exploratory experiments on the stability of mineral profiles of feathers. Journal of Wildlife Management 48:853-866.
- Eisler, R. 1985a. Cadmium hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 2. U.S. Fish and Wildlife Service Biological Report 85(1.2). Washington D.C. 92pp.
- Eisler, R. 1985b. Selenium hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 5. U.S. Fish and Wildlife Service Biological Report 85(1.5). Washington D.C. 57pp.
- Eisler, R. 1987. Mercury hazards to fish, wildlife and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 10. U.S. Fish and Wildlife Service Biological Report 85(1.10). Washington, D.C. 90pp.
- Eisler, R. 1988. Lead hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 14. U.S. Fish and Wildlife Service Biological Report 85(1.14). Washington D.C. 134pp.
- Eisler, R. 1990. Boron hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 20. U.S. Fish and Wildlife Service Biological Report 85(1.20). Washington D.C. 32pp.
- Eisler, R. 1993. Zinc hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report 26. U.S. Fish and Wildlife Service Biological Report 10. Washington D.C. 106pp.
- Franson, J.C., C.U. Meteyer and M.R. Smith. 1995. Lead poisoning of Spectacled Eider (Somateria fischeri) and of a Common Eider (Somateria mollissima) in Alaska. Journal of Wildlife Diseases 31(2):268-271.
- Furness, R.W. 1996. Cadmium in birds. *Pp* 389-404 *in* Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (eds). Environmental Contaminants in Wildlife: interpreting tissue concentrations. CRC Press, Inc., Boca Raton, FL. 494pp.

- Furness, R.W., S. J. Muirhead and M. Woodburn. 1986. Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Marine Pollution Bulletin 17:27-30.
- Goede, A.A. and M. de Bruin. 1986. The use of bird feathers for indicating heavy metal pollution. Environmental Monitoring and Assessment 7:249-256.
- Goede, A.A. and P. de Voogt. 1985. Lead and cadmium in waders from the Dutch Wadden Sea. Environmental Pollution (Series A) 37:311-322.
- Heinz, G.H. 1993. Selenium accumulation and loss in Mallard eggs. Environmental Toxicology and Chemistry 12:775-778.
- Heinz, G.H. 1996. Selenium in birds. Pp 447-4458 in Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (eds). Environmental Contaminants in Wildlife: interpreting tissue concentrations. CRC Press, Inc., Boca Raton, FL. 494pp.
- Heinz, G.H. and M.A. Fitzgerald. 1993. Reproduction of Mallards following overwinter exposure to selenium. Environmental Pollution 81:117-122.
- Heinz, G.H., D.J. Hoffman, and L.G. Gold. 1989. Impaired reproduction of Mallards fed an organic form of selenium. Journal of Wildlife Management 53:418-428.
- Henny, C.J., D.D. Rudis, T.J. Roffe and E. Robinson-Wilson. 1995. Contaminants and seaducks in Alaska and the circumpolar region. Environmental Health Perspectives 103(Suppl. 4):41-49.
- Hoffman, D.J. and G.H. Heinz. 1988. Embryonic and teratogenic effects of selenium in the diet of Mallards. Journal of Toxicology and Environmental Health 24:477-490.
- Hoffman, D.J., C.J. Sanderson, L.H. LeCaptain, E. Cromartie, and G.W. Pendleton. 1992. Interactive effects of selenium, methionine, and dietary protein on survival, growth, and physiology in Mallard ducklings. Archives of Environmental Contamination and Toxicology 23:163-171.
- Hovt, D.F. 1979. Practical methods of estimating volume and fresh weight of bird eggs. Auk 96:73-77.
- Hudec, K., F. Kredl, H. Pellantova, J. Svobodnik, and R. Svobodova. 1987. Residues of chlorinated pesticides, PCB and heavy metals in the eggs of water birds in southern Moravia. Folia Zoologica 37:157-166.
- Lande, E. 1977. Heavy metal pollution in Trondheimsfjorden, Norway, and the recorded effects on the fauna and flora. Environmental Pollution 12:187-198.
- Leonzio, C. and A. Massi. 1989. Metal biomonitoring in bird eggs: a critical experiment. Bulletin of Environmental Contamination and Toxicology 43:402-406.
- Ohlendorf, H.M. 1993. Marine birds and trace elements in the temperate North Pacific. Pp. 232-240 in Vermeer, K., K.T. Briggs, K.H. Siegel-Causey, D. (eds.). The status, ecology, and conservation of marine birds in the North Pacific. Canadian Wildlife Service Special Publications, Ottawa.
- Ohlendor, H.M. and K.C. Marois. 1991. Trace elements and organochlorines in surf scoters from San Francisco Bay, 1985. Environmental Monitoring and Assessment 18:105-122.
- Ohlendorf, H.M., R.L. Hothem, and D. Welsh. 1989. Nest success, cause-specific nest failure, and hatchability of aquatic birds at selenium-contaminated Kesterson Reservoir and a reference site. The Condor 91:787-796.

- Ohlendorf, H.M., R.W. Lowe, P.R. Kelly, and T.E. Harvey. 1986. Selenium and heavy metals in San Francisco Bay diving ducks. Journal of Wildlife Management 50:64-71.
- Pain, D.J. 1996. Lead in Waterfowl. Pp 251-264 in Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (eds). Environmental Contaminants in Wildlife: interpreting tissue concentrations. CRC Press, Inc., Boca Raton, FL. 494pp.
- Quakenbush, L.T. and E. Snyder-Conn. 1993. Pathology and contaminants case report on three Steller's Eiders from Alaska. Unpublished technical report NAES-TR-93-01, U.S. Fish and Wildlife Service, Fairbanks, AK. 32pp.
- Ruelle, R. n.d. Contaminant evaluation of interior least tern and piping plover eggs from the Missouri River in South Dakota. Unpublished report, U.S. Fish and Wildlife Service, Pierre, South Dakota. 13pp.
- Scheuhammer, A.M. 1987. The chronic toxicity of aluminum, cadmium, mercury, and lead in birds: a review. Environmental Pollution 46:263-295.
- Stickel, L.F., S.N. Wiemeyer and L.J. Blus. 1973. Pesticide residues in eggs of wild birds: adjustment for loss of moisture and lipid. Bulletin of Environmental Contamination & Toxicology...:193-196.
- Thompson, D.R. 1996. Mercury in birds and terrestrial mammals. *Pp* 341-356 *in* Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (eds). Environmental Contaminants in Wildlife: interpreting tissue concentrations. CRC Press, Inc., Boca Raton, FL. 494pp.
- Welsh, D. and P.M. Mayer. n.d. Concentrations of elements in eggs of least terms and piping plovers from the Missouri River, North Dakota. Unpublished report, U.S. Fish and Wildlife Service, Bismarck, North Dakota. 9pp.
- White, D.H. and M.T. Finley. 1978. Uptake and retention of dietary cadmium in Mallard ducks. Environmental Research 17:53-59.





For more information about the Fish and Wildlife Service in Alaska, call 888-262-6719/TDD or see our web site: http://www.r7.fws.gov

The US Department of Interior prohibits discrimination in Departmental Federally Conducted Programs on the basis of race, color, national origin, sex, age, or handicap. If you believe that you have been discriminated against in any program, activity, or facility operated by the US Fish and Wildlife Service, or if you desire further information, please write to:

US Department of the Interior Office for Equal Opportunity 1849 C Street, NW Washington, DC 20240